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Calcium stable isotopes place Devonian conodonts as first level consumers

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Abstract



Conodont animals are an extinct group of jawless vertebrates whose hard parts, also known as conodont elements, represent the earliest evidence of a mineralised skeleton in the vertebrate lineage. Conodont elements are interpreted as parts of a feeding apparatus, which together with the presence of eyes and microwear patterns, support the controversial hypothesis that conodont animals were macrophagous predators and/or scavengers. Here, we explore the trophic position of five conodont genera (*Palmatolepis*, *Polygnathus*, *Ancyrodella*, *Ancyrognathus* and *Icriodus*) from five contemporary Late Devonian sites distributed worldwide (France, Morocco, Vietnam and Australia) by means of calcium (Ca) stable isotope compositions. The seawater Ca isotope composition was calibrated using contemporary Late Devonian brachiopod isotopic values. By comparison with extant marine trophic chain composed of cartilaginous fish, conodont Ca isotope compositions are indicative of a zooplanktivore - primary piscivore niche, with

no genus-specific trophic pattern. The question of active predation or scavenging cannot be resolved definitively but our results strongly suggest that Late Devonian conodonts were first level consumers.

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Introduction

Until the publication of the discovery of the first specimen of the conodont animal in 1983 with conodont elements *in situ* forming a feeding apparatus, the nature and function of the conodont elements was one of palaeontology's great mysteries (Briggs *et al.*, 1983). Since then, several other specimens have shown similar schemes for this feeding apparatus, in which the anterior elements form a structure allowing them to trap food that is further processed by the posterior elements (Purnell and Donoghue, 1997). Today, despite the advancement of synchrotron microtomography that allows reconstructing virtual movements of the elements forming the feeding apparatus (Goudemand *et al.*, 2011), the dietary behaviour of conodonts remains an open debate but recently Shirley *et al.* (2018) suggested a predatory or scavenger mode of life. Conodonts possessed sclerotic eye capsule and extrinsic eye musculature (Gabbott *et al.*, 1995; Purnell, 1995a), consistent with conodonts having pattern vision and an active predatory lifestyle. Lastly, microwear patterns were found on conodont elements, which constituted the first direct evidence that they functioned as teeth (Purnell, 1995b).

In the present work, which is a pilot study, we use for the first time calcium (Ca) stable isotopes to infer the feeding habit

of conodont animals. The first studies showing that trophic levels of animals, including fish, could be inferred from the Ca isotope compositions of their shell or inner skeleton lay back in the 2000's (Skulan *et al.*, 1997; Skulan and DePaolo, 1999; Clementz *et al.*, 2003; DePaolo, 2004). These results were recently confirmed on modern and fossil elasmobranchs (Martin *et al.*, 2015), a subclass of cartilaginous fish, including the sharks, rays and skates, and sawfish. Some authors have already measured the Ca isotope composition of conodonts but with the aim to reconstruct variations of the seawater composition (Hinojosa *et al.* 2012; Jost *et al.* 2014; Le Houedec *et al.* 2017). Here, the Late Devonian period, particularly the Frasnian-Famennian boundary (F/F), was chosen because it is accompanied by important variations in the shape of conodont elements, suggestive of changes in the feeding behaviour of several genera (Balter *et al.*, 2008; Girard and Renaud, 2008). The Material and Method sections are described in the Supplementary Information.

Results

All values presented in this work are expressed as $\delta^{44/42}\text{Ca}$ and defined as $\delta^{44/42}\text{Ca} = ((^{44}\text{Ca}/^{42}\text{Ca}_{\text{sample}}) / (^{44}\text{Ca}/^{42}\text{Ca}_{\text{SRM915a}}) - 1) * 1000$. All measured samples were plotted as $\delta^{43/42}\text{Ca}$ against

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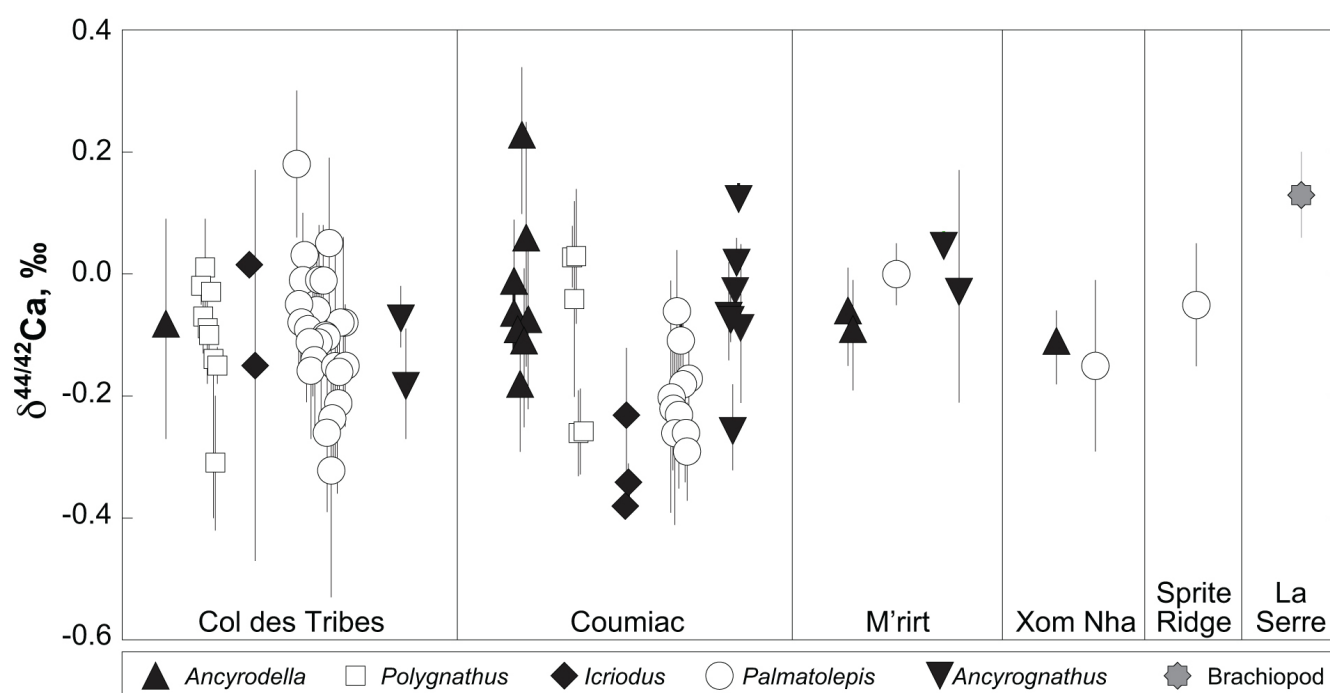


Figure 1 Ca isotope compositions of conodonts ($\delta^{44/42}\text{Ca}$) relative to SRM915a (‰) measured in the study.

$\delta^{44/42}\text{Ca}$ and fall on a line with a slope of 0.557 close to the theoretical 0.507 slope predicted by the exponential approximation of mass dependent fractionation (Tacail *et al.*, 2014; Fig. S-2). Quality control assessment is given in Table S-2, and Ca isotope values of conodonts measured in this study (Table S-3; Fig. 1) range from -0.38 ‰ to 0.22 ‰, with an average value of -0.10 ± 0.22 ‰ (± 2 s.d., $n = 80$). The average $\delta^{44/42}\text{Ca}$ value is -0.10 ± 0.20 ‰ (± 2 s.d., $n = 39$) at Col des Tribes, -0.12 ± 0.28 ‰ (± 2 s.d., $n = 39$) at Coumiac, -0.03 ± 0.12 ‰ (± 2 s.d., $n = 5$) at M'rt, -0.14 ± 0.04 ‰ (± 2 s.d., $n = 2$) at Xom Nha and -0.05 ‰ at Sprite Ridge (Table S-3). Comparison between conodonts at Coumiac and Col des Tribes, the two most abundant sites, reveals no significant difference of the $\delta^{44/42}\text{Ca}$ value (Student's *t*-test, $p = 0.373$). Comparisons between conodonts grouped by genus reveal no taxonomic difference (Table S-4). The brachiopod yielded a $\delta^{44/42}\text{Ca}$ value of 0.13 ‰ (Table S-1), which represents one of the highest values of the dataset.

Discussion

The present paper focuses on the trophic position of conodont animals based on their Ca isotope compositions, but these could have been affected by diagenetic processes. Discussion on the effects of diagenesis is developed in the Supplementary Information. We conclude, in the absence of any evidence of Ca isotope compositions being diagenetically reworked, that the measured $\delta^{44/42}\text{Ca}$ values of conodonts are biogenic.

The present paper focuses on the trophic position of conodont animals based on their Ca isotope composition, but accurate comparisons with modern analogues first necessitate calibrating the Ca isotopic values of the conodont elements relative to that of the contemporaneous seawater. Based on the existing Ca isotopic fractionation factor between modern brachiopods (br) *Terebratalia* and seawater (sw), $\alpha_{\text{br-sw}} = 0.99915$ (Gussone *et al.*, 2005), the $\delta^{44/42}\text{Ca}$ value of end-Devonian seawater ($\delta^{44/42}\text{Ca}_{\text{sw}}$) was estimated at 0.55 ‰, *i.e.* ~ 0.4 ‰ lower than that of modern oceans (Blättler *et al.* 2012). With an age estimated slightly younger than the Devonian-Carboniferous boundary of 360 Ma, this value falls in the range, but

in the lower limit, of the reconstructed Phanerozoic seawater Ca isotope composition of Farkaš *et al.* (2007; Fig. S-3). We can now calculate the Ca isotopic offset between seawater and conodonts, which is equal to 0.65 ± 0.25 ‰, (\pm s.d., $n = 80$). Conodonts are made up of hydroxylapatite (hap), which is more or less fluorinated, but it is the same mineral phase as that of elasmobranch teeth. This allows comparing the average Ca isotopic offset between Devonian seawater and conodonts with that of modern seawater and extant elasmobranch tooth enameloid (Martin *et al.* 2015), which is annotated $\Delta^{44/42}\text{Ca}_{\text{sw-hap}}$ (Fig. 2). Using a modern seawater $\delta^{44/42}\text{Ca}_{\text{sw}}$ value of 0.92 ‰, an offset of ~ 0.65 ‰ is observed nowadays between seawater and the zooplanktivore and primary piscivore group, which are characterised by average $\Delta^{44/42}\text{Ca}_{\text{sw-hap}}$ values of 0.56 ± 0.27 ‰ (± 2 s.d., $n = 5$) and 0.86 ± 0.08 ‰ (± 2 s.d., $n = 6$), respectively (Fig. 2). To fully encompass the $\delta^{44/42}\text{Ca}_{\text{sw}}$ variability at that time, which is well described by the study of Farkaš *et al.* (2007), we can also calculate the $\Delta^{44/42}\text{Ca}_{\text{sw-hap}}$ with the upper limit of the contemporaneous $\delta^{44/42}\text{Ca}_{\text{sw}}$ value, *i.e.* ~ 0.67 ‰. Even with this higher value, the calculated $\Delta^{44/42}\text{Ca}_{\text{sw-hap}}$ offset shows that conodonts are still in the the zooplanktivore - primary piscivore group (Fig. 2). The observation that conodonts fall as first level consumers is in accordance with the macrophagous hypothesis (*i.e.* feeding on relatively large particles of food), but is at odds with the view that conodont animals had a purely predatory lifestyle, which would have implied a $\delta^{44/42}\text{Ca}$ value of conodont elements around 1 ‰. Scavenging of fish cannot be ruled out, but must have involved small fish above all, otherwise the $\delta^{44/42}\text{Ca}$ values would have been those of predators.

Another argument in favour of a basal trophic position for conodonts, is that modern piscivore elasmobranchs exhibit a much tighter grouping of the $\delta^{44/42}\text{Ca}$ values than modern zooplanktivore elasmobranchs and conodonts (Figs. 1 and 2). The range of $\delta^{44/42}\text{Ca}$ values for a given trophic level of piscivore elasmobranchs never exceeds 0.1 ‰ while it is higher than 0.2 ‰ for modern zooplanktivore elasmobranchs and conodonts. No definitive explanation can be put forward from the state of the results, but a reasonable hypothesis could be that animals at the bottom of the trophic chain are more likely to sample local isotopic heterogeneities. This variability

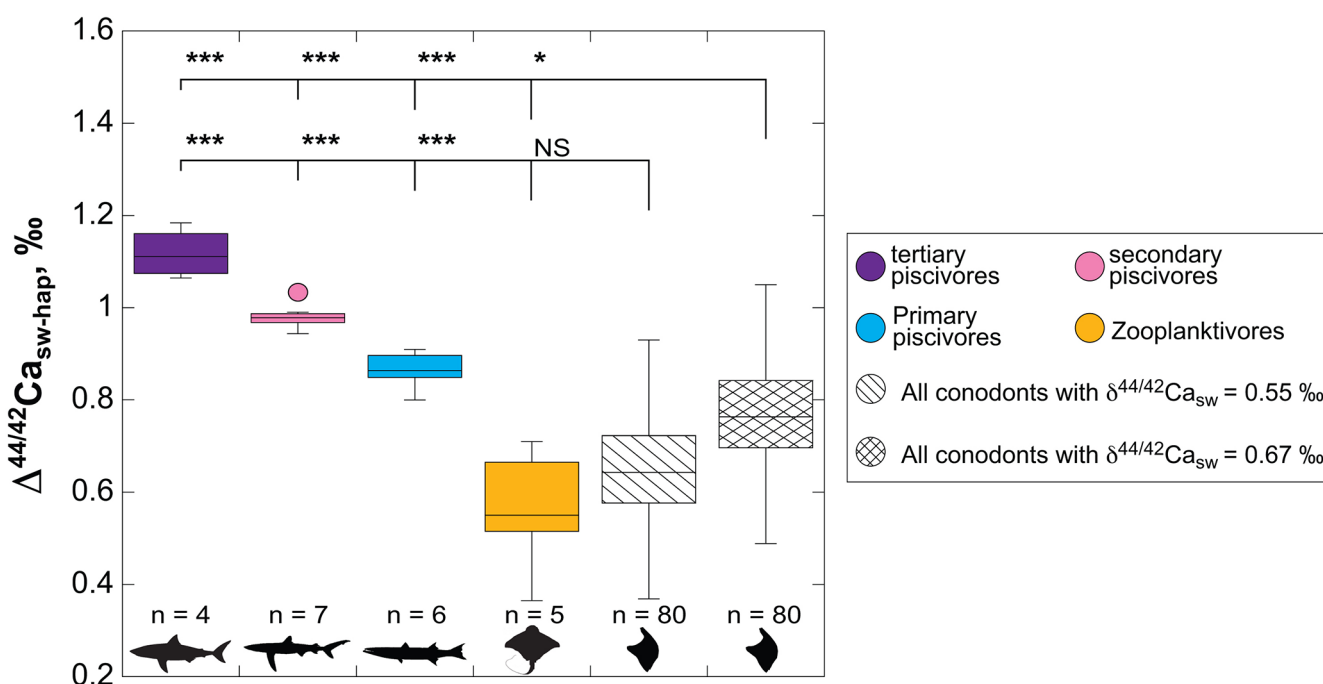


Figure 2 Ca isotopic offset between seawater and hap of modern elasmobranchs compared to that of conodonts ($\Delta^{44/42}\text{Ca}_{\text{sw-hap}}$) measured in the study. Modern elasmobranch data are from Martin *et al.* (2015). The $\Delta^{44/42}\text{Ca}_{\text{sw-hap}}$ offset is calculated with two $\delta^{44/42}\text{Ca}_{\text{sw}}$ values, 0.55 ‰ (diagonal lines) and 0.67 ‰ (diagonal cross hatch) corresponding to the range given by Farkaš *et al.* (2007; Fig. S-3). Boxplots delimit 5, 25, 50, 75 and 95 % percentiles. Depending on the $\delta^{44/42}\text{Ca}_{\text{sw}}$ value, statistics show that conodonts and zooplanktivores have similar $\delta^{44/42}\text{Ca}$ values. Under the null hypothesis that there is no difference in the distribution of two groups of $\delta^{44/42}\text{Ca}$ values, the p value of Student's t-tests provides the smallest level of significance at which null hypothesis would be rejected (NS, non-significant p value; *p = 0.01–0.05; **p = 0.001–0.01; and ***p < 0.001).

is subsequently contracted at higher trophic level probably thanks to a biopurification process such as in the case of the Sr/Ca and Ba/Ca ratios (Peek and Clementz, 2012).

The present results suggest that no significant difference in trophic level may have existed among conodonts, because genera exhibit indistinguishable $\delta^{44/42}\text{Ca}$ values (Table S-2). This overall similarity suggests that competition must have existed between some genera occupying similar trophic levels at the same time, *i.e.* between *Palmatolepis* and *Polygnathus* for instance. It is noteworthy that *Ancyrodella* is the only genus analysed in the study that disappeared at the F/F boundary, questioning the possibility that a distinct ecological trait would have triggered the extinction of this conodont genus.

Using a similar $\Delta^{44/42}\text{Ca}_{\text{sw-hap}}$ for conodont elements and modern elasmobranchs to retrieve the trophic position of conodont animals implies similar vital effects (*i.e.* isotope fractionation due to biological processes) in both groups. This approach is however probably simplistic. In fish, Ca is taken up along three pathways, (1) directly from the water *via* the gills, which contain a lot of ion-transporting cells or chloride cells (also known as ionocytes), but also through the intestine from (2) drinking water and (3) food (Flik and Verboost, 1993). No evidence for gills has ever been reported in preserved specimens of conodont animals (Aldridge and Purnell, 1996), which would suggest distinct $\Delta^{44/42}\text{Ca}_{\text{sw-hap}}$ values between conodont animals and elasmobranchs. Total intestinal absorption of calcium in marine fish represents around 30 % of the total calcium intake (Björnsson and Nilsson, 1985; Sundell and Björnsson, 1988). To our knowledge, relative proportions of drinking water and food in fish have never been determined, but the isotopic results of Martin *et al.* (2015) in elasmobranchs demonstrate that food must make a sizable proportion, otherwise no trophic effect would have been observed. Indeed, the most likely explanation to account for the depletion of Ca heavy isotopes up trophic chains, being marine or terrestrial, is that preys are wholly ingested along with their skeleton

which is depleted in heavy Ca isotopes. If the three types of Ca uptake described above are characterised by different isotope fractionation intensity, and their relative proportions vary between fish groups, this should in principle result in a different $\Delta^{44/42}\text{Ca}_{\text{sw-hap}}$ fractionation. Analysis of dietary relevant trace elements for marine organisms, such as Sr/Ca and Ba/Ca ratios (Balter and Lécuyer, 2004, 2010; Le Houedec *et al.*, 2013; Peek and Clementz, 2012) would corroborate the present results, but we question whether this would be feasible in light of the difference of vital effects discussed above, and of potential diagenetic effects. Further analysis of Ca isotopes in conodont assemblages will document the diversity of their ecological niches within Palaeozoic oceanic trophic chains.

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Additional Information

Supplementary Information accompanies this letter at <http://www.geochemicalperspectivesletters.org/article1912>.



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